

- 1 1. A biodegradable polyurethane composite, comprising:
2 a polyurethane matrix formed by reaction of a polyisocyanate with an optionally
3 hydroxylated biomolecule to form a biodegradable polyurethane polymer;
4 and
5 a reinforcement embedded in the matrix, wherein the reinforcement comprises a
6 material selected from the group consisting of bone and bone substitutes.

- 7 2. The polyurethane composite of claim 1, wherein the reinforcement comprises a
8 material selected from the group consisting of calcium carbonate, calcium sulfate,
9 calcium phosphosilicate, sodium phosphate, calcium aluminate, calcium
10 phosphate, calcium carbonate, hydroxyapatite, demineralized bone, mineralized
11 bone, and combinations and modified forms of the above.

- 12 3. The polyurethane composite of claim 1, wherein the biodegradable polyurethane
13 polymer is cross-linked.

- 14 4. The polyurethane composite of claim 1, wherein the polyisocyanate is a
15 diisocyanate.

- 16 5. The polyurethane composite of claim 1, wherein the polyisocyanate is selected
17 from the group consisting of lysine diisocyanate, toluene diisocyanate, arginine
18 diisocyanate, asparagine diisocyanate, glutamine diisocyanate, hexamethylene
19 diisocyanate, hexane diisocyanate, methylene bis-p-phenyl diisocyanate,
20 isocyanurate polyisocyanates, 1,4-butane diisocyanate, uretdione polyisocyanate,
21 and aliphatic, alicyclic, and aromatic polyisocyanates.

- 22 6. The polyurethane composite of claim 1, wherein the biomolecule is selected from
23 the group consisting of phospholipids, fatty acids, cholesterols, polysaccharides,
24 starches, and combinations and modified forms of the above.

- 25 7. The polyurethane composite of claim 1, wherein the biomolecule is lecithin.

- 1 8. The polyurethane composite of claim 1, further comprising polycaprolactone.
- 2 9. The polyurethane composite of claim 1, further comprising one or more
- 3 substances selected from a biomolecule, a bioactive agent, and a small molecule.
- 4 10. The polyurethane composite of claim 9, wherein the substance is selected from
- 5 the group consisting of lectins, growth factors, immunosuppressives, and
- 6 chemoattractants.
- 7 11. The polyurethane composite of claim 1, comprising at least 10 weight percent of
- 8 the reinforcement.
- 9 12. The polyurethane composite of claim 1, comprising at least 30 weight percent of
- 10 the reinforcement.
- 11 13. The polyurethane composite of claim 1, comprising at least 50 weight percent of
- 12 the reinforcement.
- 13 14. The polyurethane composite of claim 1, comprising at least 70 weight percent of
- 14 the reinforcement.
- 15 15. The polyurethane composite of claim 1, wherein the polyurethane composite has a
- 16 wet compressive strength that exceeds the wet compressive strength of the
- 17 polyurethane alone.
- 18 16. The polyurethane composite of claim 1, wherein the polyurethane composite has a
- 19 wet compressive strength of at least 3 MPa.
- 20 17. The polyurethane composite of claim 1, wherein the polyurethane composite has a
- 21 wet compressive strength of at least 10 MPa.
- 22 18. The polyurethane composite of claim 1, wherein the polyurethane composite has a
- 23 wet compressive strength of at least 50 MPa.

1 19. The polyurethane composite of claim 1, wherein the polyurethane composite has a
2 wet compressive strength of at least 75 MPa.

3 20. The polyurethane composite of claim 1, wherein the polyurethane composite has a
4 wet compressive strength of at least 100 MPa.

5 21. The polyurethane composite of claim 1, wherein the polyurethane composite does
6 not fail when subjected to at least 10^5 fatigue cycles at 3 MPa when wet.

7 22. The polyurethane composite of claim 1, wherein the polyurethane composite does
8 not fail when subjected to at least 10^6 fatigue cycles at 25 MPa when wet.

9 23. The polyurethane composite of claim 1, wherein the polyurethane has a creep rate
10 of less than 15% in 24 hours at 3 MPa when wet.

11 24. The polyurethane composite of claim 1, wherein the polyurethane has a creep rate
12 of less than 10% in 24 hours at 25 MPa when wet.

13 25. The polyurethane composite of claim 1, wherein the polyurethane degrades at a
14 rate sufficient to permit generation of new tissue at an *in vivo* implantation site.

15 26. The polyurethane composite of claim 1, wherein the polyurethane degrades at a
16 rate of about 5% of original composite weight per month when implanted *in vivo*.

17 27. The polyurethane composite of claim 1, wherein the polyurethane degrades at a
18 rate of about 10% of original composite weight per month when implanted *in*
19 *vivo*.

20 28. The polyurethane composite of claim 1, wherein the polyurethane degrades at a
21 rate of about 25% of original composite weight per month when implanted *in*
22 *vivo*.

23 29. The polyurethane composite of claim 1, wherein the polyurethane has a maximum
24 resolved shear strength of at least 3 MPa.

1 30. The polyurethane composite of claim 1, wherein the polyurethane has a maximum
2 resolved compressive strength of at least 3 MPa.

3 31. The polyurethane composite of claim 1, wherein the polyurethane has a maximum
4 resolved tensile strength of at least 3 MPa.

5 32. A biodegradable polyurethane, formed by reaction of a polyisocyanate with a
6 mixture of optionally hydroxylated biomolecules to form a polyurethane polymer,
7 wherein the mixture of optionally hydroxylated biomolecules comprises
8 polysaccharides; and
9 lipids or phospholipids.

10 33. The polyurethane of claim 32, wherein the polymer is cross-linked.

11 34. The polyurethane of claim 32, wherein the polyisocyanate is a diisocyanate.

12 35. The polyurethane of claim 32, wherein the polyisocyanate is selected from the
13 group consisting of lysine diisocyanate, toluene diisocyanate, arginine
14 diisocyanate, asparagine diisocyanate, glutamine diisocyanate, hexamethylene
15 diisocyanate, hexane diisocyanate, methylene bis-p-phenyl diisocyanate,
16 isocyanurate polyisocyanates, 1,4-butane diisocyanate, uretdione polyisocyanate,
17 and aliphatic, alicyclic, and aromatic polyisocyanates.

18 36. The polyurethane of claim 32, wherein the mixture of biomolecule comprises
19 lecithin.

20 37. The polyurethane of claim 32, further comprising polycaprolactone.

21 38. The polyurethane of claim 32, further comprising a substance selected from a
22 biomolecule, a bioactive agent, and a small molecule.

23 39. The polyurethane of claim 38, wherein the substance is selected from the group
24 consisting of lectins, growth factors, immunosuppressives, and chemoattractants.

1 40. The polyurethane of claim 32, further comprising a reinforcement embedded in a
2 matrix of the polyurethane to form a composite material.

3 41. The polyurethane of claim 40, wherein the reinforcement comprises a material is
4 selected from the group consisting of calcium carbonate, calcium sulfate, calcium
5 phosphosilicate, sodium phosphate, calcium aluminate, calcium phosphate,
6 calcium carbonate, hydroxyapatite, demineralized bone, mineralized bone, and
7 combinations and modified forms of the above.

8 42. The polyurethane of claim 40, comprising at least 10 weight percent of the
9 reinforcement.

10 43. The polyurethane of claim 40, comprising at least 30 weight percent of the
11 reinforcement.

12 44. The polyurethane of claim 40, comprising at least 50 weight percent of the
13 reinforcement.

14 45. The polyurethane of claim 40, comprising at least 70 weight percent of the
15 reinforcement.

16 46. The polyurethane of claim 40, wherein the composite material has a wet
17 compressive strength that exceeds the wet compressive strength of the
18 polyurethane alone.

19 47. The polyurethane of claim 32, wherein the polyurethane has a wet compressive
20 strength of at least 3 MPa.

21 48. The polyurethane of claim 32, wherein the polyurethane has a wet compressive
22 strength of at least 10 MPa.

23 49. The polyurethane of claim 32, wherein the polyurethane has a wet compressive
24 strength of at least 50 MPa.

- 1 50. The polyurethane of claim 32, wherein the polyurethane has a wet compressive
2 strength of at least 75 MPa.
- 3 51. The polyurethane of claim 32, wherein the polyurethane has a wet compressive
4 strength of at least 100 MPa.
- 5 52. The polyurethane of claim 32, wherein the polyurethane does not fail when
6 subjected to at least 10^5 fatigue cycles at 3 MPa when wet.
- 7 53. The polyurethane of claim 32, wherein the polyurethane does not fail when
8 subjected to at least 10^6 fatigue cycles at 25 MPa when wet.
- 9 54. The polyurethane of claim 32, wherein the polyurethane has a creep rate of less
10 than 15% in 24 hours at 3 MPa when wet.
- 11 55. The polyurethane of claim 32, wherein the polyurethane has a creep rate of less
12 than 10% in 24 hours at 25 MPa when wet.
- 13 56. The polyurethane of claim 32, wherein the polyurethane degrades at a rate
14 sufficient to permit generation of new tissue at an *in vivo* implantation site.
- 15 57. The polyurethane of claim 32, wherein the polyurethane degrades at a rate of
16 about 5% of its original weight per month when implanted *in vivo*.
- 17 58. The polyurethane of claim 32, wherein the polyurethane degrades at a rate of
18 about 10% of its original weight per month when implanted *in vivo*.
- 19 59. The polyurethane of claim 32, wherein the polyurethane degrades at a rate of
20 about 25% of its original weight per month when implanted *in vivo*.
- 21 60. The polyurethane of claim 32, wherein the polyurethane has a maximum resolved
22 shear strength of at least 3 MPa.

1 61. The polyurethane of claim 32, wherein the polyurethane has a maximum resolved
2 compression strength of at least 3 MPa.

3 62. The polyurethane of claim 32, wherein the polyurethane has a maximum resolved
4 tensile strength of at least 3 MPa.

5 63. A polyurethane, formed by reaction of a polyisocyanate with a biomolecule to
6 form a nonresorbable, biocompatible polyurethane polymer, wherein the
7 biomolecule comprises a polysaccharide.

8 64. The polyurethane of claim 63, wherein the polyurethane is formed by reaction of
9 the polyisocyanate with the polysaccharide and with a lipid or phospholipid.

10 65. The polyurethane of claim 63, wherein the polymer is cross-linked.

11 66. The polyurethane of claim 63, wherein the polyisocyanate is a diisocyanate.

12 67. The polyurethane of claim 63, wherein the polyisocyanate is selected from the
13 group consisting of lysine diisocyanate, toluene diisocyanate, arginine
14 diisocyanate, asparagine diisocyanate, glutamine diisocyanate, hexamethylene
15 diisocyanate, hexane diisocyanate, methylene bis-p-phenyl diisocyanate,
16 isocyanurate polyisocyanates, 1,4-butane diisocyanate, uretdione polyisocyanate,
17 and aliphatic, alicyclic, and aromatic polyisocyanates.

18 68. The polyurethane of claim 63, wherein the mixture of biomolecule comprises
19 lecithin.

20 69. The polyurethane of claim 63, further comprising polycaprolactone.

21 70. The polyurethane of claim 63, further comprising a substance selected from a
22 biomolecule, a bioactive agent, and a small molecule.

23 71. The polyurethane of claim 70, wherein the substance is selected from the group
24 consisting of lectins, growth factors, immunosuppressives, and chemoattractants.

1 72. The polyurethane of claim 63, further comprising a reinforcement embedded in a
2 matrix of the polyurethane to form a composite material.

3 73. The polyurethane of claim 72, wherein the reinforcement comprises a material is
4 selected from the group consisting of calcium carbonate, calcium sulfate, calcium
5 phosphosilicate, sodium phosphate, calcium aluminate, calcium phosphate,
6 calcium carbonate, hydroxyapatite, demineralized bone, mineralized bone, and
7 combinations and modified forms of the above.

8 74. The polyurethane of claim 72, comprising at least 10 weight percent of the
9 reinforcement.

10 75. The polyurethane of claim 72, comprising at least 30 weight percent of the
11 reinforcement.

12 76. The polyurethane of claim 72, comprising at least 50 weight percent of the
13 reinforcement.

14 77. The polyurethane of claim 72, comprising at least 70 weight percent of the
15 reinforcement.

16 78. The polyurethane of claim 72, wherein the composite material has a wet
17 compressive strength that exceeds the wet compressive strength of the
18 polyurethane alone.

19 79. The polyurethane of claim 63, wherein the polyisocyanate reacts with a hydroxyl
20 group on the biomolecule.

21 80. A method of making a polyurethane composite, comprising:
22 reacting a polyisocyanate with an optionally hydroxylated biomolecule and a
23 reinforcement to form a biodegradable polyurethane polymer matrix
24 having particles of reinforcement embedded therein,

1 wherein the reinforcement comprises a material is selected from the group
2 consisting of bone and bone substitutes.

3 81. The method of claim 80, wherein the reinforcement comprises a material selected
4 from the group consisting of calcium carbonate, calcium sulfate, calcium
5 phosphosilicate, sodium phosphate, calcium aluminate, calcium phosphate,
6 calcium carbonate, hydroxyapatite, demineralized bone, mineralized bone, and
7 combinations and modified forms of the above.

8 82. The method of claim 80, further comprising adding a substance selected from a
9 bioactive agent, a biomolecule, and a small molecule material to the composite.

10 83. The method of claim 82, wherein the substance is selected from the group
11 consisting of lectins, growth factors, immunosuppressives, and chemoattractants.

12 84. The method of claim 80, wherein reacting further comprises adding a chain
13 extender.

14 85. The method of claim 80, wherein reacting comprises:
15 reacting the polyisocyanate and the biomolecule to form a prepolymer;
16 mixing the prepolymer with the reinforcement to form a precomposite; and
17 reacting the precomposite to form the polyurethane composite.

18 86. The method of claim 85, wherein reacting the precomposite comprises cross-
19 linking the prepolymer.

20 87. The method of claim 80, wherein reacting comprises reacting for a time period
21 from about one minute to about four hours.

22 88. The method of claim 80, wherein reacting comprises exposing the polyisocyanate
23 and the biomolecule to a catalyst.

1 89. The method of claim 88, wherein the catalyst comprises a material selected from
2 the group consisting of mild bases, strong bases, sodium hydroxide, sodium
3 acetate, tin, and triethylene diamine 1,4 diazo(2,2,2) bicyclooctane.

4 90. A method of making a biodegradable polyurethane, comprising:
5 reacting a polyisocyanate with a mixture of optionally hydroxylated biomolecules
6 to form a polyurethane polymer, wherein the mixture of optionally
7 hydroxylated biomolecules comprises
8 polysaccharides; and
9 lipids or phospholipids.

10 91. The method of claim 90, further comprising adding a reinforcement to the
11 polyurethane polymer to form a composite material.

12 92. The method of claim 91, wherein the reinforcement is selected from the group
13 consisting of calcium carbonate, calcium sulfate, calcium phosphosilicate, sodium
14 phosphate, calcium aluminate, calcium phosphate, calcium carbonate,
15 hydroxyapatite, demineralized bone, mineralized bone, and combinations and
16 modified forms of the above.

17 93. The method of claim 91, wherein reacting comprises:
18 reacting the polyisocyanate and the biomolecule to form a prepolymer;
19 mixing the prepolymer with the reinforcement to form a precomposite; and
20 reacting the precomposite to form the polyurethane composite.

21 94. The method of claim 93, wherein reacting the precomposite comprises cross-
22 linking the prepolymer.

23 95. The method of claim 90, further comprising adding a substance selected from a
24 bioactive agent, a biomolecule, and a small molecule to the polymer.

25 96. The method of claim 95, wherein the substance is selected from the group
26 consisting of lectins, growth factors, immunosuppressives, and chemoattractants.

1 97. The method of claim 90, wherein reacting further comprises adding a chain
2 extender.

3 98. The method of claim 90, wherein reacting comprises reacting for a time period
4 from about one minute to about four hours.

5 99. The method of claim 90, wherein reacting comprises exposing the polyisocyanate
6 and the biomolecule to a catalyst.

7 100. The method of claim 98, wherein the catalyst comprises a material selected from
8 the group consisting of mild bases, strong bases, sodium hydroxide, sodium
9 acetate, tin, and triethylene diamine 1,4 diazo(2,2,2) bicyclooctane.

10 101. A method of making a polyurethane, comprising
11 reacting a polyisocyanate with a biomolecule to form a nonresorbable,
12 biocompatible polyurethane polymer, wherein the biomolecule comprises
13 a polysaccharide.

14 102. The method of claim 100, further comprising adding a reinforcement to the
15 polyurethane polymer to form a composite material.

16 103. The method of claim 102, wherein the reinforcement is selected from the group
17 consisting of calcium carbonate, calcium sulfate, calcium phosphosilicate, sodium
18 phosphate, calcium aluminate, calcium phosphate, calcium carbonate,
19 hydroxyapatite, demineralized bone, mineralized bone, and combinations and
20 modified forms of the above.

21 104. The method of claim 102, wherein reacting comprises:
22 reacting the polyisocyanate and the biomolecule to form a prepolymer;
23 mixing the prepolymer with the reinforcement to form a precomposite; and
24 reacting the precomposite to form the polyurethane composite.

1 105. The method of claim 104, wherein reacting the precomposite comprises cross-
2 linking the prepolymer.

3 106. The method of claim 100, further comprising adding a substance selected from a
4 bioactive agent, a biomolecule, and a small molecule to the polymer.

5 107. The method of claim 100, wherein the substance is selected from the group
6 consisting of lectins, growth factors, immunosuppressives, and chemoattractants.

7 108. The method of claim 100, wherein reacting further comprises adding a chain
8 extender.

9 109. The method of claim 100, wherein reacting comprises reacting for a time period
10 from about one minute to about four hours.

11 110. The method of claim 100, wherein reacting comprises exposing the
12 polyisocyanate and the biomolecule to a catalyst.

13 111. The method of claim 109, wherein the catalyst a material selected from the group
14 consisting of mild bases, strong bases, sodium hydroxide, sodium acetate, tin, and
15 triethylene diamine 1,4 diazo(2,2,2) bicyclooctane.